

AN ABSTRACT OF THE THESIS OF

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Title: HOMOLYTIC AROMATIC SUBSTITUTION. SUBSTITUENT
EFFECTS IN THE RADICAL TRICHLOROMETHYLATION OF
9-X-ANTHRACENES

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Gerald Jay Gleicher

The reaction rates of the trichloromethyl radical addition to a series of 9-substituted anthracenes relative to trans-stilbene have been determined at 70.0°. It is demonstrated that there is a definite substituent dependence for this addition reaction, and that when the logarithms of the relative rates are plotted vs. Brown's σ_p^+ substituent parameters for the 9-X-anthracenes, good correlation is obtained ($r = 0.970$) with $\rho^+ = -0.83$. Significant deviations from this correlation are observed for two types of compounds. The deviation for compounds such as 9-nitroanthracene is explained in terms of steric inhibition of resonance. Compounds with readily abstractable hydrogen atoms such as 9-methylantracene tend to undergo appreciable side-chain reaction.

Homolytic Aromatic Substitution. Substituent Effects
in the Radical Trichloromethylation of
9-X-Anthracenes

by

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Associate Professor of Chemistry

in charge of major

Redacted for Privacy

Chairman of Department of Chemistry

Redacted for Privacy

Dean of Graduate School

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Typed by Clover Redfern for James Charles Arnold

To my wife

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
Statement of the Problem	11
RESULTS AND DISCUSSION	13
Synthesis of the 9-Substituted Anthracenes	13
Kinetic Studies: Relative Rates of Disappearance of 9-Substituted Anthracenes Relative to <u>trans</u> -Stilbene	13
Analysis of the Results	16
EXPERIMENTAL	25
Purification of Reagents	25
Purification of Bromotrichloromethane	25
Purification of Benzene	25
Purification of <u>p</u> -Dibromobenzene	26
Purification of <u>trans</u> -Stilbene	26
Purification of Benzoyl Peroxide	26
Purification of Anthracene	26
Purification of 9-Bromoanthracene	26
Purification of 9-Methylantracene	27
Preparation of Compounds	27
Preparation of 9-Chloroanthracene	27
Preparation of 9-Cyanoanthracene	27
Preparation of 9-Methoxyanthracene	28
Preparation of Methyl 9-Anthroate	28
Preparation of 9-Nitroanthracene	28
Preparation of the 9-Alkylantracenes	29
Kinetic Studies	29
Procedure for Kinetic Runs	29
Determination of k_X/k_{Std}	30
BIBLIOGRAPHY	31
APPENDIX	35

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Relative rates of disappearance of 9-substituted anthracenes <u>vs.</u> <u>trans</u> -stilbene toward trichloromethyl radical addition at 70.0°.	15
2. Relative rates of disappearance of 9-substituted anthracenes <u>vs.</u> anthracene toward trichloromethyl radical addition at 70.0°.	16
3. Relative rates of disappearance of 9-nitroanthracene to <u>trans</u> -stilbene.	35
4. Relative rates of disappearance of 9-cyanoanthracene to <u>trans</u> -stilbene.	36
5. Relative rates of disappearance of methyl 9-anthroate to <u>trans</u> -stilbene.	37
6. Relative rates of disappearance of 9-bromoanthracene to <u>trans</u> -stilbene.	38
7. Relative rates of disappearance of 9-chloroanthracene to <u>trans</u> -stilbene.	39
8. Relative rates of disappearance of anthracene to <u>trans</u> -stilbene.	40
9. Relative rates of disappearance of 9-phenylanthracene to <u>trans</u> -stilbene.	41
10. Relative rates of disappearance of 9-isopropylanthracene to <u>trans</u> -stilbene.	42
11. Relative rates of disappearance of 9-ethylanthracene to <u>trans</u> -stilbene.	43
12. Relative rates of disappearance of 9-methylanthracene to <u>trans</u> -stilbene.	44
13. Relative rates of disappearance of 9-methoxyanthracene to <u>trans</u> -stilbene.	45

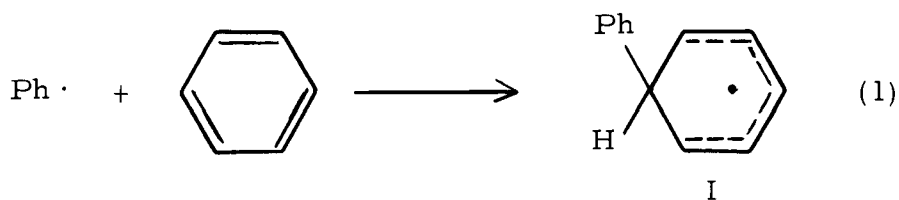
HOMOLYTIC AROMATIC SUBSTITUTION. SUBSTITUENT
EFFECTS IN THE RADICAL TRICHLOROMETHYLATION
OF 9-X-ANTHRACENES

INTRODUCTION

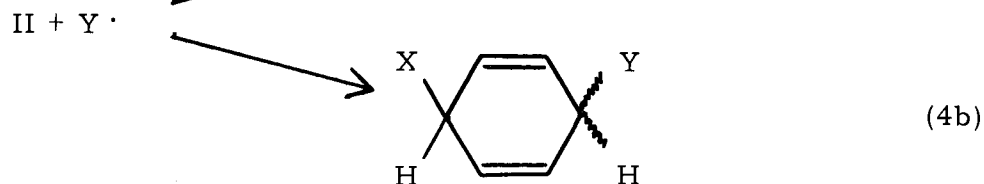
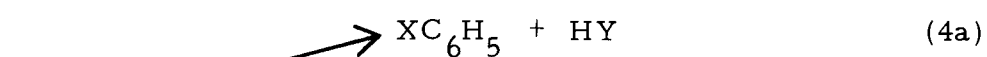
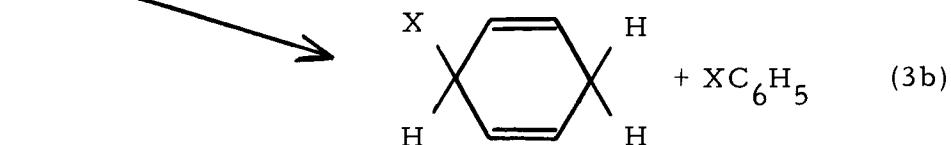
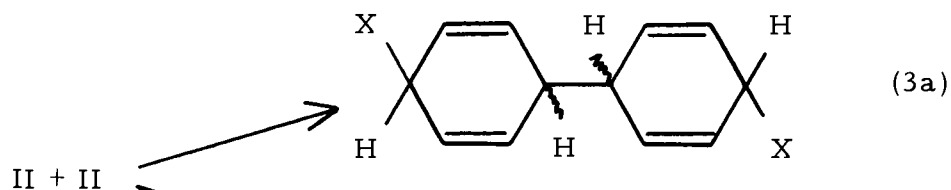
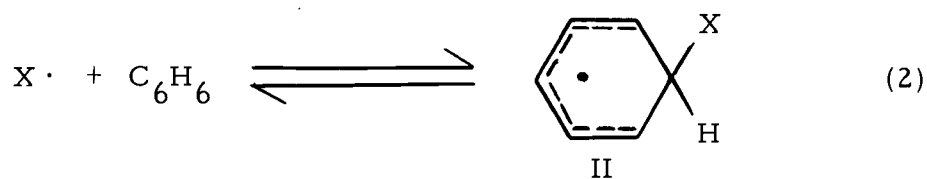
The relative reactivities of a series of arylmethanes toward hydrogen atom abstraction by the trichloromethyl radical have been studied by Unruh and Gleicher (1,2). The kinetics for the 13 compounds studied exhibited a rate spread of approximately three powers of ten. The reactivities were not only dependent upon the aryl portion of the molecule but also upon the position of the methyl group; the three methylanthracenes had, for example, a rate spread of about 20. Experimentally it was known, however, that the course of reaction of this series of compounds was not clean. The methylarenes could undergo a reaction by attack of the trichloromethyl radical upon the cyclic portion of the molecule. The problem of such a competing process in a study of this type was most clearly demonstrated when a series of arylmethanes was subjected to hydrogen abstraction by bromine atom (3). Gilliom and coworkers found that compounds which were anthracene or pyrene derivatives did not afford side-chain bromination products. Rather a rapid reaction apparently occurred in the cyclic portion of the molecule. These considerations led to an interest in possible homolytic aromatic substitution in general and the reactions of polycyclic aromatic systems with the trichloromethyl

radical in particular.

By far the most studied homolytic aromatic substitution reaction is that of phenylation. As early as 1934 Grieve and Hey suggested that the reactive species involved in the phenylation of aromatic substrates, both in the Gomberg reaction and in reactions of nitrosoacetanilide, was a free phenyl radical (4). In 1937 Hey and Waters further elaborated upon this suggestion in an important review (5). In 1941 Waters formulated the initial act in the substitution process as addition to the aromatic ring (6).



However, it seems to have been another 15 years before the full range of chemical behavior of the product of addition, namely the phenylcyclohexadienyl radical (I) was properly appreciated (7). Since then, reactions of a variety of radicals with a range of aromatic substrates have been investigated, and the following general scheme may now be written in which benzene is a representative substrate. The initially formed cyclohexadienyl radical (II), formed by the addition of $X \cdot$, may undergo dimerization (3a) or disproportionation (3b), or with radical $Y \cdot$, undergo hydrogen abstraction (4a) or radical combination (4b). Along with the types of products pictured below, products



arising from ortho coupling or disproportionation in one or both rings also occur (analogous to reactions 3a, 3b and 4b). This general reaction scheme, then, outlines the scope of the possible reaction pathways involving radical addition to an aromatic ring.

In an early investigation on the process of radical addition to polycyclic aromatics, Kooyman and Farenhorst studied the addition of the trichloromethyl radical to *n*-hexadecene and styrene (8). They found that these reactions were retarded by added aromatic hydrocarbon and from the extent of retardation were able to estimate the relative rates of reactivities of the various aromatics toward the

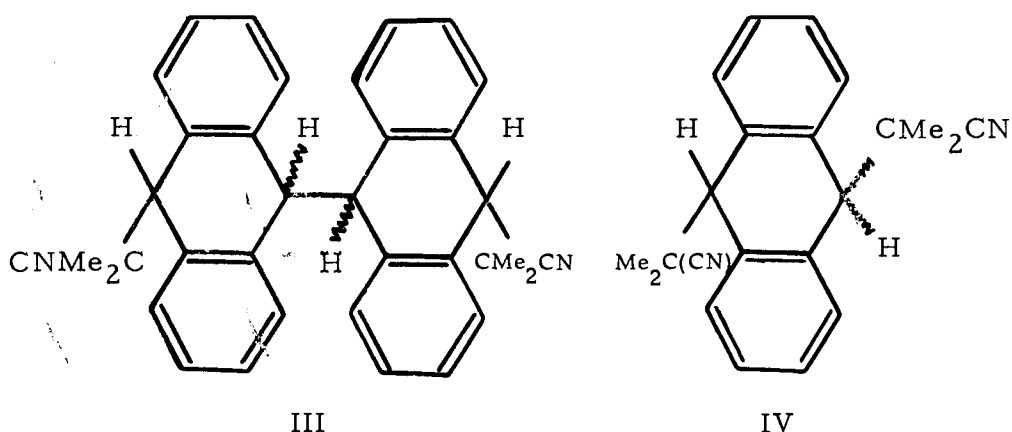
trichloromethyl radical. It was found that an approximate linear relationship held between the logarithms of the relative rate constants and the maximum free valencies (F_{\max} , as calculated by a Hückel molecular orbital approach) for the respective aromatic compounds. In a related study, Levy and Szwarc developed a method for determining the reactivities of methyl radicals toward a series of aromatic hydrocarbons (9). A plot of the logarithms of the relative rate constants of trichloromethyl radical addition (8) vs. the logarithms of the relative rates of methyl radical addition resulted in a linear relationship. It followed, therefore, that the same type of linear relation must hold for the logarithms of methyl radical addition relative reactivities and F_{\max} . The existence of such a relationship implies that radicals add to that particular carbon atom in the systems corresponding to F_{\max} (9).

More recent work has given similar correlations. It has been found that phenyl radicals, generated under the conditions of the Meerwein reaction, react with naphthalene and anthracene to give product distributions much as expected from radical localization energy considerations (10). Naphthalene yields 87% alpha phenylation; anthracene yields 84% of the 9-phenyl product. Further substantiation to the above was detailed in a theoretical study (11). Dewar and Thompson have shown that an excellent linear relationship exists between the logarithms of the relative rates of methyl

radical addition (9) and radical localization energies for free-radical substitution (i. e. , the pi energy difference of the radical sigma complexes and the parent arenes, calculated by a SCF-LCAO-MO approach). While the relative rate data can be correlated with the free valence index (8,9), the more significant correlation with radical localization energies exists (11). The correlation with localization energy has been advocated as providing the best theoretical measure of the reactivity of a position toward free radicals (12). This conclusion must be viewed as being based on the fact that the localization energy is a term which reflects an energy difference between radical intermediate and ground state, not on ground state energy alone. In correlating the rates of radical formation with the differences in pi-binding energies between the intermediate addition products (i. e. , sigma complexes) and the starting arene reactant, the Hammond postulate (13) demands that the transition states must resemble the sigma complexes.

The free-radical chemistry of anthracene and its derivatives, with which this report deals, has not been a neglected area of research. Radical addition to acene systems is relatively facile, the loss of resonance energy being small compared with that in the addition to other aromatics. The anthracene system is a case in point. Here, products arising from ortho disproportionation or coupling are not formed. The products which are formed should not be particularly

susceptible to further radical attack. Thus, Bickel and Kooyman have reported that both III and IV are among the products of reaction of cyanoisopropyl radicals with anthracene (14). Compound III is a



characteristic product of the dimerization reaction (3a), and IV a result of a radical combination reaction (4b) with the initially formed intermediate. Many other products of addition to the anthracene nucleus by the relatively unreactive radicals $\text{PhCH}_2\cdot$ (15, 16), $\text{PhCO}\cdot$ (17), $\text{RS}\cdot$ (18), and $\text{PhSO}_2\cdot$ (19), have been subsequently identified.

The extent of competing ring substitution with the hydrogen abstraction process in the reaction of the trichloromethyl radical with arylmethanes was faced by Unruh and Gleicher (1, 2). The effect of the methyl group with respect to its influence on the substitution reaction was quantitatively unknown. In a qualitative manner, however, the available data in the literature was used as a guide. The effects of substituents in the reaction of anthracene derivatives with

trichloromethyl (20, 22) and cyanoisopropyl (21, 22) radicals were apparently quite small and the reactivities did not seemingly vary in a regular sense with the electronic character of the substituent. This data was similar to that obtained in the phenylation reactions of a series of substituted benzenes (23). Regardless of phenyl radical source or substituent on the benzene ring, a rate enhancement, compared to benzene, was observed. Unruh and Gleicher, therefore, made the assumption that 9-methylantracene and anthracene would show approximately the same tendency to undergo ring reaction per active position. Competitive reactions between anthracene and 9-methylantracene were utilized to determine the extent of hydrogen abstraction in the latter system. The same technique was extended to determine the extent of hydrogen abstraction in the other arylmethanes as well. Despite the use of this approach, however, the possibility that substituent groups could play a distinct systematic role in determining the course of radical substitution in these systems would seem quite reasonable. This possibility, apparently contradicted experimentally by Farenhorst and Kooyman (21, 22), was also at odds with the results of some MO calculations which indicated that any substituent, regardless of its electronic nature, should favor ring reaction (24). It had been reasoned by Greenwood that the free valence of atom 10 of the anthracene nucleus increases in passing from the parent hydrocarbon to any of the 9-substituted derivatives and should be

paralleled by an increase in reactivity at this position. Of course this argument need not necessarily hold true if indeed radical localization energies, rather than F_{\max} , are viewed as a better index for correlation.

It has long been known that substituent groups can play a part in influencing the course of organic reactions. Hammett-type correlations (25) which relate structure and reactivity of organic substrates to yield linear free energy relationships are, indeed, quite common to free-radical as well as ionic reactions. For example, the effects of ring substitution on hydrogen abstraction from substituted toluenes using bromine atoms (26,27) and the trichloromethyl radical (28) have been examined. The effects of substituents in this system were quite pronounced, electron withdrawing substituents retarding the rates of reaction and electron donating substituents enhancing the rates. Of interest in this case is the fact that the relative rates of both the bromine atom and trichloromethyl radical hydrogen abstraction reactions correlated with the σ^+ substituent parameters of Brown and Okamoto (29). This implies that there exists a fairly high degree of polar character associated with the transition state for this process. Similar σ^+ correlations have also been observed in the hydrogen abstraction reactions of substituted ethylbenzenes (30), cumenes (31), neopentylbenzenes (32), and benzyl chlorides (33). These studies have shown that both electron density and potential steric interactions

at the reaction site are important in determining how sensitive the aromatic substrates are to changes in substituents on the ring.

Recent studies have also been reported which show definite substituent dependence on the reactivities of substituted benzenes toward various radical additions. The most extensive single set of results on phenylation measured under comparable conditions is probably that of Simamura and coworkers (34). These were obtained by isotope dilution analysis of the products of thermolysis of p-substituted N-nitrosoacetanilides in mixtures of benzene and its derivatives. The rates of attack at the meta positions of substituted benzenes showed good correlations with Hammett's σ constants, the rho values of which revealed a pronounced polarization in phenyl radicals carrying a para substituent. The figures for attack at the para position were correlated satisfactorily only after the introduction of a parameter, τ_p , according to the relationship

$$\log k_p/k = \rho\sigma_p + \tau_p .$$

The τ_p values derived were essentially constant for a particular substituent group in the substrate and were taken to represent the ability of the substituent to stabilize the intermediate radical by a direct conjugative effect. The same approach was used for attack at the ortho position. The τ_o values, however, were much larger in

magnitude in order to give a satisfactory correlation. This would seem to suggest that the τ_o values are not only associated with the conjugative effect of the substituent group but also with a corresponding steric effect.

Pryor and coworkers have also used the Hammett equation in correlating the addition of tritium atoms to substituted benzenes (35). The tritium atoms were generated by photolyzing a solution of tritium-labeled thiophenol and the substituted benzenes. The distribution of the tritium in the recovered aromatic was then determined and from this the rate data was accumulated. A plot of the partial rate factors for meta attack vs. σ_m and for para attack vs. σ_p yielded a reasonable correlation, although the ρ value was small (-0.24) and the error limits in comparison somewhat large (standard deviation from ρ was ± 0.09).

If these recent observations for definite substituent effects in the radical additions to substituted benzenes carry over in the same manner to substituted polycyclic aromatics, older results on substituent effects in the anthracene system (20,21,22) should be viewed as suspect. Also to be considered are the results of the MO calculations of Greenwood, already mentioned, which predict rate increases for substituted anthracenes (24). For highly exothermic reactions, where the transition state resembles closely the ground state, F_{\max} may indeed possess certain advantages in correlating radical

reactions. In an endothermic process, where the transition state must necessarily more closely resemble the radical intermediate, radical localization energies should provide a more meaningful correlation.

Statement of the Problem

The research to be described herein has attempted to obtain some definitive answers to the problem of substituent effects in the radical addition reactions of polycyclic aromatic compounds. It was anticipated that a study of this type would determine whether any serious error had been incorporated into the work of Unruh and Gleicher on their study of hydrogen abstraction from arylmethanes (1, 2) by the approach then utilized. Also, since it is generally acknowledged that polar effects accompany the reactions of the trichloromethyl radical, it would be expected that a regular variation of the reactivity with the electronic character of the substituent should be evident.

This report deals with a study undertaken to examine the effects of substituents in the radical trichloromethylation of 9-substituted anthracenes. This series of compounds was chosen for a variety of reasons. Anthracenes should be appreciably more susceptible to substituent effects than other common polynuclear aromatic systems (36). With respect to the possible sites of radical attack, the relatively high

reactivity of the meso positions should increase the selectivity of the overall process. Also, anthracene should undergo reaction toward the trichloromethyl radical at rates about 10^5 that of benzene, 3×10^3 that of chrysene, and approximately 3×10^2 that of pyrene with respect to the most active sites in each molecule (8). Unless abstractable hydrogen atoms are present, the anthracene derivatives should react almost solely in the meso positions. Based upon kinetic results and the argument that a substituent should exercise a retarding steric effect, Kooyman predicted that 9-substituted anthracenes should preferentially react in the 10 position (20, 21, 22). A recent CIDNP investigation of the addition of the cyanoisopropyl radical to 9-bromoanthracene shows this definitely to be the case (37).

The research described in this report includes synthesis of the substituted anthracenes, the kinetic studies of these compounds in reaction with the trichloromethyl radical, and the correlation of the relative rates of reaction with Brown's σ_p^+ parameters.

RESULTS AND DISCUSSION

Synthesis of the 9-Substituted Anthracenes

9-Chloroanthracene, 9-cyanoanthracene, 9-methoxy-anthracene, 9-nitroanthracene, 9-ethylanthracene, 9-isopropyl-anthracene, 9-phenylanthracene, and methyl 9-anthroate were synthesized by methods in the literature. Anthracene, 9-bromo-anthracene, and 9-methylanthracene were obtained commercially. Details regarding the synthesis and/or purification of these compounds may be found in the Experimental section.

Kinetic Studies: Relative Rates of Disappearance of 9-Substituted Anthracenes Relative to trans-Stilbene

The addition reactions of the trichloromethyl radical toward the series of 9-substituted anthracenes were run in replicate relative to trans-stilbene. Reactions were carried out in sealed ampoules under a reduced pressure of nitrogen at $70.0 \pm 0.2^\circ\text{C}$. The solvent was a benzene-bromotrichloromethane mixture, used to insure solubility of the substrates. Benzene and bromotrichloromethane were maintained at a constant mole to mole ratio of 3:2 throughout all kinetic runs. Possible changes in complexation factors of the trichloromethyl radical with solvent (38) affecting the rates were thereby avoided. The radical initiator was benzoyl peroxide.

Although recently the identity of the chain carrying species has come into question in photolytic hydrogen abstractions involving bromotrichloromethane (39), the trichloromethyl radical is believed to be the reactive radical species in this study just as in the additions of bromotrichloromethane to double bonds (40). Hey and coworkers have shown that, in the absence of oxygen, the phenyl radical (generated from the peroxide decomposition) abstracts bromine atom from bromotrichloromethane almost exclusively (41, 42). Since no hydrogen bromide should be produced in the present reaction, the possibility of the reaction of the trichloromethyl radical with HBr to give chloroform and bromine atom is viewed as extremely remote.

Solubility problems made direct competition between two anthracene derivatives prohibitive; this was overcome by having an anthracene derivative and trans-stilbene compete directly for the trichloromethyl radical. The addition of bromotrichloromethane to the intercylic double bond of stilbenes is known to proceed smoothly (43). The relative rates of disappearance of substituted anthracenes to trans-stilbene were determined via gas-liquid chromatography. Full details regarding the kinetic determinations are outlined in the Experimental section. Table 1 gives the reactivities of the substituted anthracenes relative to trans-stilbene. Table 2 shows these results converted so that all reactivities are expressed relative to anthracene. Also listed in Table 2 are the σ_p^+ parameters of Brown and Okamoto

(29) for the various substituent groups.

Table 1. Relative rates of disappearance of 9-substituted anthracenes vs. trans-stilbene toward trichloromethyl radical addition at 70.0°. ^a

Substituent	k_X/k_{Std}	Number of Kinetic Runs
NO ₂	1.61 ± 0.23 ^b	7
CN	0.77 ± 0.09	5
CO ₂ CH ₃	1.68 ± 0.16	5
Br	2.25 ± 0.10	7
Cl	2.31 ± 0.09	7
H	2.26 ± 0.42 ^c	7
C ₆ H ₅	5.17 ± 0.98	7
<i>i</i> -C ₃ H ₇	5.39 ± 0.69	6
C ₂ H ₅	7.66 ± 1.00	10
CH ₃	15.50 ± 2.01	6
OCH ₃	12.47 ± 1.36	5

^aComplete data for the kinetic runs may be found in the Appendix.

^bAverage deviation.

^cStatistically corrected.

Table 2. Relative rates of disappearance of 9-substituted anthracenes vs. anthracene toward trichloromethyl radical addition at 70.0°.

Substituent	k_X/k_H	σ_p^+ <u>a/</u>
NO ₂	0.71 ± 0.10	0.790
CN	0.34 ± 0.04	0.659
CO ₂ CH ₃	0.74 ± 0.07	0.489
Br	1.00 ± 0.04	0.150
Cl	1.02 ± 0.04	0.114
H	1.00	0
C ₆ H ₅	2.28 ± 0.43	-0.179
<u>i</u> -C ₃ H ₇	2.38 ± 0.30	-0.280
C ₂ H ₅	3.39 ± 0.44	-0.295
CH ₃	6.85 ± 0.89	-0.311
OCH ₃	5.52 ± 0.60	-0.778

a/ From reference 29.

Analysis of the Results

As can be seen from the results presented in Tables 1 and 2, the rates of reaction of the trichloromethyl radical toward the anthracenes are affected by the nature of the substituent. Anthracenes with electron donating substituents show enhanced rates and those with electron withdrawing substituents show retarded rates relative to the parent hydrocarbon. Figure 1 shows a graphical representation of these results presented in the form of a linear free energy

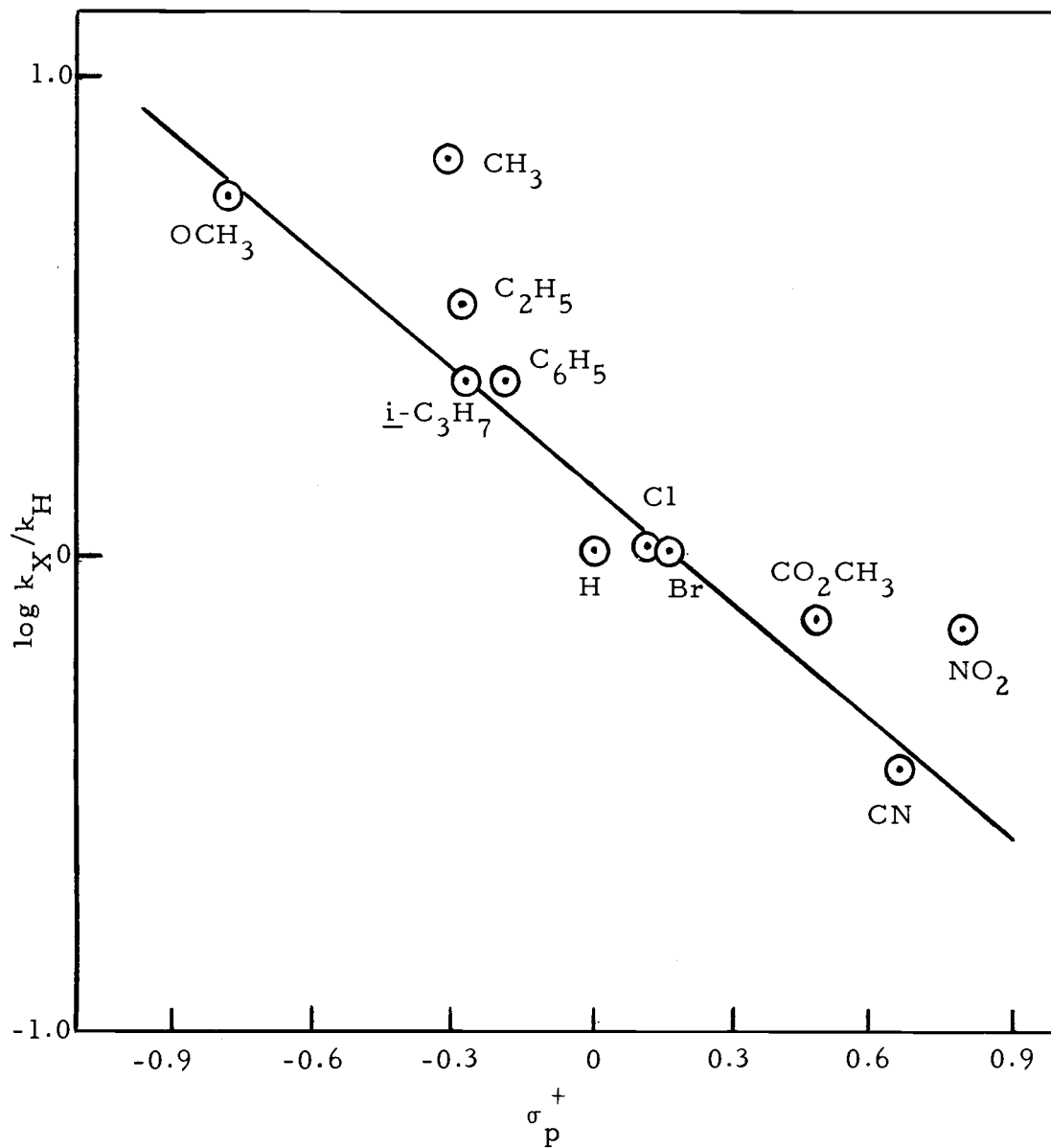


Figure 1. Correlation of $\log k_X/k_H$ and σ_p^+ for the radical trichloromethylation of 9-substituted anthracenes.

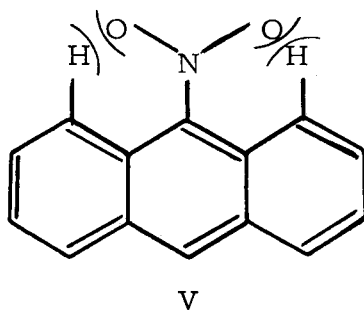
relationship. The logarithms of the relative rates of reaction are plotted against the σ_p^+ parameters of Brown and Okamoto (29). The same function is almost universally encountered in correlations of the formation of benzylic type radicals. It would seem logical to expect these parameters to be operative in all cases, such as the present study, where direct resonance interaction between the substituent and the site of radical formation can occur. Utilizing nine of the eleven points (excluding nitro and methyl) a linear relationship is obtained with a slope (ρ^+) of -0.83 and a good correlation coefficient of 0.970. The ρ^+ value appears quite reasonable and comparable in magnitude to that found for hydrogen abstractions from substituted allylbenzenes, -0.64 (44), a system where resonance stabilization of the resultant radicals by substituents is not unlike that in the present situation.

The deviation of the methyl and nitro points from the correlation line is deemed of considerable interest. The methyl compound exhibits the highest reactivity of all the compounds in the series. This is interpreted as due to loss of material via hydrogen abstraction from the exocyclic methyl position as well as ring substitution. The present correlation estimates the relative amounts of side-chain reaction and ring reaction to be 65% and 35% respectively. The previously reported values by Unruh and Gleicher on their study of arylmethanes (1,2) were 83% and 17%. In that study the logarithms of the relative

rates of hydrogen abstraction from the arylmethanes were plotted against the change in pi-binding energy between the arylmethyl radicals and the parent arenes as calculated by a SCF-LCAO-MO approach. This yielded a line with slope +5.45 and correlation coefficient of 0.977. With the correction from this work incorporated into that study, the slope of the correlation line is changed to +5.34 with a correlation coefficient of 0.973. The overall change introduced into that linear free energy relationship, therefore, is of the order of two percent. It is felt that this should have been the largest source of error which was incorporated into that work, and the findings of this study show that those results are not significantly affected.

It is felt that the upward deviation of 9-nitroanthracene from the correlation line is a result of steric inhibition of resonance. The nitro group is necessarily treated as an electron withdrawing substituent by virtue of both inductive and resonance criteria. The latter, however, demands a coplanarity of the aryl and nitro moieties. While it has been shown that nitrobenzene is planar in the crystal (45), complete coplanarity is absent in the p-dinitrobenzene system (46). In the latter compound the angle of inclination of the nitro groups toward the benzene ring is 9.5° . This should still, however, allow for extensive delocalization. Such should not be the case for 9-nitroanthracene. Non-bonded interactions between the nitro group and the hydrogen atoms at positions 1 and 8 (see structure V) should

definitely preclude coplanarity. In a planar structure a distance of only approximately 1.70 \AA would be found between the oxygen atoms of the nitro group and the peri hydrogens. An X-ray structure determination on 9-nitroanthracene by Trotter has shown that in the solid phase



the nitro group is nearly perpendicular (85°) to the aromatic system (47). Although Trotter has subsequently argued that a less severe deviation from planarity might exist in solution (48), it must be concluded that much of the electron withdrawing tendencies of the nitro group are not present in this molecule. With the effect of the nitro group diminished in this way, 9-nitroanthracene exhibits a much larger relative rate than would be expected.

It should be noted that substituents in other 9-substituted anthracenes also deviate appreciably from planarity. Both carbomethoxy and methoxy are far from coplanar with the anthracene system, the deviations being 73° and 86° respectively (49).

Carbomethoxy should qualitatively resemble nitro in its electronic properties and it does show a slight upward deviation from the

correlation line. While this may be due to some steric inhibition of resonance, the departure from the correlation is approximately within the experimental uncertainty. Therefore, the results for methyl 9-anthroate have been treated as representing a "normal" effect. The electronic properties of the methoxy group differ greatly from the others just discussed in possessing a resonance effect which is electron donating. Though nonplanarity should theoretically remove this effect, the kinetic results show no departure from expectation. The nonplanar structure does not preclude potential resonance stabilization, however. The pi system of electrons of the aromatic could now interact with the lone pair of electrons in the oxygen hybrid orbital. This interaction should be substantial and it is felt that this is the reason for the expected behavior of the methoxy compound.

The phenyl group in 9-phenylanthracene is also most likely out of the plane of the anthracene system. Here again, electron release should not be as effective as if the phenyl group were coplanar. However, the good correlation obtained is not unexpected since the reaction series used to develop the σ_p^+ values (29) most probably had the phenyl substituent in a noncoplanar arrangement also. Indeed, a recent report in the literature shows that a new σ_p^+ value has been developed for phenyl in a known coplanar arrangement (50). The greater negative value assigned to σ_p^+ for phenyl in that situation indicates that a planar phenyl group is more electron releasing than a methyl, a situation

which does not exist in the present study.

In addition to the analysis of the reactivity of 9-methylanthracene, the reactivities of the two other 9-alkylanthracenes merit some comment. As stated, 9-methylanthracene apparently undergoes a considerable amount of hydrogen abstraction from the exocyclic methyl accounting for a large portion of its reactivity. The formation of the benzylic type radical in this process necessarily leads to a situation where peri interactions between the exocyclic hydrogen atoms and the hydrogen atoms in positions 1 and 8 may occur. This type of interaction may cause lessened stabilization of the radical intermediate due to a loss of coplanarity of the exocyclic position with respect to the anthracene system. It has been shown, however, that these unfavorable interactions in the 1-methylnaphthalene case may be lessened by in-plane bending deformations at both the exocyclic carbon and the carbon to which it is attached along with an out-of-plane deformation of one hydrogen at the exocyclic site and an opposite such deformation at the peri position (51). A somewhat analogous situation may exist in the case of 9-methylanthracene, allowing significant hydrogen abstraction even though two peri hydrogen atoms exist. Increasing alpha substitution yielding the cases of 9-ethyl and 9-isopropylanthracene makes much more significant the problem of peri interactions and the very large probability that these two compounds undergo hydrogen abstraction to only a very small extent.

This is, in essence, substantiated by including these compounds in the overall correlation and noting only very small deviations from the relation obtained. Indeed, preliminary strain energy calculations show that a planar radical intermediate resulting in hydrogen abstraction from 9-isopropylanthracene has a prohibitively large non-bonded interaction strain term. In addition, the more strain-free perpendicular structure allows for no radical delocalization into the anthracene nucleus. Figure 1 shows that the reactivity of 9-isopropylanthracene is essentially that of a compound undergoing only the radical addition process. The point for 9-ethylanthracene is slightly more off the correlation line; this may be an indication that a small amount of this material is reacting via the hydrogen abstraction process. These results are qualitatively in accord with a study reported on the free-radical halogenation of 9-alkyl and 9-arylanthracenes with iodobenzene dichloride (52) which yielded similar relative rate data for the three alkylanthracenes which have been included in this study. In that case also, the methyl compound was much more reactive than the other two alkyl systems.

In conclusion it has been shown that the good correlation of relative rates of reaction with the σ_p^+ substituent parameters is compatible with the idea that polar effects accompany the reactions of the trichloromethyl radical, even in the case of a polycyclic aromatic

system. Also, it has been demonstrated that only small error was introduced into the work of Unruh and Gleicher on arylmethanes (1, 2) by the assumptions which had then been made.

EXPERIMENTAL

Melting points were taken in unsealed capillary tubes with a Mel-Temp melting point apparatus and are uncorrected. Gas-liquid chromatography analyses were carried out with a Varian Aerograph 202-B gas chromatograph equipped with thermal conductivity detectors, a linear temperature programmer, and a Hewlett Packard 337B digital integrator. The column used in this research was a 12 ft. by 0.25 in. aluminum column of 5% SE-30 on Chromosorb W. Helium gas was utilized as the eluent.

Purification of Reagents

Purification of Bromotrichloromethane

GLC showed only trace amounts of impurities in reagent grade bromotrichloromethane (Matheson Coleman and Bell). The reagent was dried over anhydrous magnesium sulfate and distilled at atmospheric pressure. After discarding the first ten percent of the distillate, a constant-boiling fraction was collected and stored in an amber bottle.

Purification of Benzene

Reagent grade benzene was washed with concentrated sulfuric acid, followed by distilled water, and dried over anhydrous magnesium

sulfate. It was then distilled; the first 20 percent of the distillate was discarded. The purified benzene was stored over a large amount of sodium ribbon.

Purification of p-Dibromobenzene

Commercial p-dibromobenzene (Matheson Coleman and Bell) was used without further purification; m. p. 87-88°.

Purification of trans-Stilbene

Commercial trans-stilbene (Matheson Coleman and Bell, Scintillation Grade) was used with no further purification; m. p. 124-125°.

Purification of Benzoyl Peroxide

Grannular benzoyl peroxide (Matheson Coleman and Bell) was used without further purification.

Purification of Anthracene

Commercial anthracene (Aldrich) of 99.9% purity was used without further purification; m. p. 215-217°.

Purification of 9-Bromoanthracene

Commercial 9-bromoanthracene (Aldrich) was used with no

further purification; m. p. 94-97°. GLC analysis showed purity in excess of 99%.

Purification of 9-Methylantracene

Commercial 9-methylantracene (Aldrich) was used with no further purification; m. p. 78-79°.

Preparation of Compounds

Preparation of 9-Chloroanthracene

9-Chloroanthracene was prepared from the reaction of anthracene and anhydrous cupric chloride in refluxing carbon tetrachloride (53). The product was purified by elution through an alumina column with carbon tetrachloride. After evaporation of the solvent, 9-chloroanthracene (79.5%) gave lemon-yellow crystals, m. p. 98-100°, lit. 104-106°. No impurities were detected by gas-liquid chromatography.

Preparation of 9-Cyanoanthracene

9-Anthraldehyde (Columbia) was converted to the oxime by the reaction with hydroxylamine hydrochloride in ethanol. Dehydration of the oxime was effected by refluxing in acetic anhydride. 9-Cyanoanthracene was obtained as long yellow needles which were

recrystallized from glacial acetic acid, m.p. 177-178°, lit. 177.5-179° (54). No impurities could be detected by gas-liquid chromatography.

Preparation of 9-Methoxyanthracene

9-Methoxyanthracene was obtained from the reaction of anthrone and aqueous sodium hydroxide, followed by the addition of methyl *p*-toluenesulfonate according to the method of Meek and coworkers (55). The product which was isolated was repeatedly recrystallized from isopropanol to a constant m.p. of 94-96°, lit. 95-96°. No impurities were detected by gas-liquid chromatography.

Preparation of Methyl 9-Anthroate

Methyl 9-anthroate was prepared by the reaction of 9-anthroic acid with methanol, in benzene and trifluoroacetic anhydride, according to the method of Parish and Stock (56). The product was recrystallized once from methanol yielding an orange-yellow solid, m.p. 111-112°, lit. 112.7-113.2° (57). The yield was 72.9%. No impurities were detected by gas-liquid chromatography.

Preparation of 9-Nitroanthracene

9-Nitroanthracene was prepared by the direct nitration of anthracene with nitric acid according to a standard procedure (58).

The product was recrystallized from glacial acetic acid yielding orange-yellow needles, m. p. 142-144°, lit. 145-146°. No impurities were detected by gas-liquid chromatography.

Preparation of the 9-Alkylanthracenes

The reaction of anthrone with the appropriate alkyl magnesium halide was utilized to prepare the 9-alkylanthracenes according to the method of Klemm and coworkers (59). The initially formed products of this reaction underwent spontaneous dehydration, yielding the desired products: 9-ethylanthracene, m. p. 54.5-56.5, lit. 59° (60), 9-isopropylanthracene, m. p. 76-77°, lit. 75-76°, and 9-phenylanthracene, m. p. 148.5-151.5, lit. 152-153° (61). No impurities could be detected in these compounds upon analysis by gas-liquid chromatography.

Kinetic Studies

Procedure for Kinetic Runs

A solution of the substituted anthracene, trans-stilbene, p-dibromobenzene, bromotrichloromethane, and benzene was prepared in the approximate molar ratio of 1:2:1:50:75. A small amount was reserved for analysis as starting material. The remainder was divided among ampoules containing a small amount of benzoyl peroxide.

The ampoules were sealed under a reduced pressure of nitrogen and then placed in a constant temperature bath at $70.0^\circ \pm 0.2^\circ$. After completion of the reaction, the ampoules were cooled and opened and analyzed for the disappearance of the substituted anthracene and trans-stilbene via GLC using p-dibromobenzene as an internal standard.

Determination of k_X/k_{Std}

The ratios of relative rate constant were obtained using established competitive procedures (28, 31). The relative rate of disappearance for the substituted anthracene (k_X) and trans-stilbene (k_{Std}) is given by:

$$(k_X/k_{Std})_{dis} = \frac{\log(X_i/X_f)}{\log(Std_i/Std_f)}$$

where $(k_X/k_{Std})_{dis}$ is the relative rate of disappearance of the substrates, X_i and Std_i are the number of mmoles originally present of substituted anthracene and trans-stilbene; X_f and Std_f are the corresponding terms for the final number of mmoles present. The above ratio may be directly obtained from the chromatographic analysis using the following relationship:

$$\frac{X_i}{X_f} = \frac{\left[\frac{\text{area under X peak}}{\text{area under p-dibromobenzene peak}} \right]_{\text{initial}}}{\left[\frac{\text{area under X peak}}{\text{area under p-dibromobenzene peak}} \right]_{\text{final}}}$$

Detailed kinetic data may be found in the Appendix.

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APPENDIX

Table 3. Relative rates of disappearance of 9-nitroanthracene to trans-stilbene.

Conditions: 114.5 hrs at 70.0°
 Initial mmoles BrCCl₃: 25.01
 Mmoles benzene: 37.64
 Mmoles p-dibromobenzene: 0.5544

Run No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% r x n	$\frac{k_{9\text{-Nitroanth}}}{k_{\text{trans-Stilbene}}}$
1	9-Nitroanth	0.5344	0.3567	0.1777	33.25	1.623
	<u>trans</u> -Stilbene	0.9986	0.7785	0.2201	22.04	
2	9-Nitroanth	0.5344	0.3649	0.1695	31.71	1.635
	<u>trans</u> -Stilbene	0.9986	0.7908	0.2078	20.81	
3	9-Nitroanth	0.5344	0.3640	0.1704	31.88	1.231
	<u>trans</u> -Stilbene	0.9986	0.7310	0.2686	26.80	
4	9-Nitroanth	0.5344	0.3047	0.2297	42.99	2.032
	<u>trans</u> -Stilbene	0.9986	0.7573	0.2413	24.16	
5	9-Nitroanth	0.5344	0.3844	0.1500	28.06	1.963
	<u>trans</u> -Stilbene	0.9986	0.8444	0.1542	15.44	
6	9-Nitroanth	0.5344	0.3072	0.2272	42.52	1.456
	<u>trans</u> -Stilbene	0.9986	0.6826	0.3160	31.64	
7	9-Nitroanth	0.5344	0.3562	0.1782	33.34	1.317
	<u>trans</u> -Stilbene	0.9986	0.7340	0.2646	26.50	

$$\text{Average } \frac{k_{9\text{-Nitroanth}}}{k_{\text{trans-Stilbene}}} = 1.61 \pm 0.23$$

Table 4. Relative rates of disappearance of 9-cyanoanthracene to trans-stilbene.

Conditions: 100.5 hrs at 70.0°
 Initial mmoles BrCCl₃: 25.10
 Mmoles benzene: 37.68
 Mmoles p-dibromobenzene: 0.5570

Run No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% r x n	$\frac{k_{9\text{-Cyanoanth}}}{k_{\text{trans-Stilbene}}}$
1	9-Cyanoanth	0.5240	0.4516	0.0724	13.82	0.850
	<u>trans</u> -Stilbene	0.9981	0.8379	0.1602	16.05	
2	9-Cyanoanth	0.5240	0.3798	0.1442	27.51	0.865
	<u>trans</u> -Stilbene	0.9981	0.6882	0.3099	31.05	
3	9-Cyanoanth	0.5240	0.4518	0.0722	13.78	0.613
	<u>trans</u> -Stilbene	0.9981	0.7837	0.2144	21.48	
4	9-Cyanoanth	0.5240	0.4188	0.1052	20.08	0.702
	<u>trans</u> -Stilbene	0.9981	0.7250	0.2731	27.36	
5	9-Cyanoanth	0.5240	0.3682	0.1558	29.74	0.836
	<u>trans</u> -Stilbene	0.9981	0.6544	0.3437	34.33	
Average		$\frac{k_{9\text{-Cyanoanth}}}{k_{\text{trans-Stilbene}}} = 0.77 \pm 0.09$				

Table 5. Relative rates of disappearance of methyl 9-anthroate to trans-stilbene.

Conditions: 98.5 hrs at 70.0°
 Initial mmoles BrCCl₃: 25.07
 Mmoles benzene: 37.56
 Mmoles p-dibromobenzene: 0.5192

Run No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% r x n	$\frac{k_{\text{Methyl 9-Anthroate}}}{k_{\text{trans-Stilbene}}}$
1	Methyl 9-Anthroate	0.5110	0.3713	0.1397	27.33	1.698
	<u>trans</u> -Stilbene	1.030	0.8534	0.1765	17.14	
2	Methyl 9-Anthroate	0.5110	0.3775	0.1335	26.13	2.053
	<u>trans</u> -Stilbene	1.030	0.8887	0.1413	13.72	
3	Methyl 9-Anthroate	0.5110	0.3996	0.1114	21.81	1.547
	<u>trans</u> -Stilbene	1.030	0.8785	0.1515	14.71	
4	Methyl 9-Anthroate	0.5110	0.4221	0.0889	17.39	1.417
	<u>trans</u> -Stilbene	1.030	0.9001	0.1299	12.61	
5	Methyl 9-Anthroate	0.5110	0.4002	0.1108	21.69	1.695
	<u>trans</u> -Stilbene	1.030	0.8917	0.1383	13.43	
Average						$\frac{k_{\text{Methyl 9-Anthroate}}}{k_{\text{trans-Stilbene}}} = 1.68 \pm 0.16$

Table 6. Relative rates of disappearance of 9-bromoanthracene to trans-stilbene.

Conditions: 96.5 hrs at 70.0°
 Initial mmoles BrCCl₃: 25.30
 Mmoles benzene: 38.15
 Mmoles p-dibromobenzene: 0.5171

Run No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% r x n	$\frac{k_{9\text{-Bromoanth}}}{k_{\text{trans-Stilbene}}}$
1	9-Bromoanth	0.5394	0.4343	0.1050	19.48	2.515
	<u>trans</u> -Stilbene	1.004	0.9579	0.0861	8.25	
2	9-Bromoanth	0.5394	0.3890	0.1504	27.88	2.143
	<u>trans</u> -Stilbene	1.004	0.8964	0.1476	14.14	
3	9-Bromoanth	0.5394	0.4113	0.1281	23.74	2.337
	<u>trans</u> -Stilbene	1.004	0.9297	0.1143	10.95	
4	9-Bromoanth	0.5394	0.3720	0.1674	31.04	2.258
	<u>trans</u> -Stilbene	1.004	0.8855	0.1585	15.18	
5	9-Bromoanth	0.5394	0.3941	0.1453	26.93	2.074
	<u>trans</u> -Stilbene	1.004	0.8974	0.1466	14.04	
6	9-Bromoanth	0.5394	0.3763	0.1631	30.23	2.227
	<u>trans</u> -Stilbene	1.004	0.8882	0.1558	14.92	
7	9-Bromoanth	0.5394	0.4301	0.1093	20.26	2.207
	<u>trans</u> -Stilbene	1.004	0.9422	0.1018	9.75	
Average $\frac{k_{9\text{-Bromoanth}}}{k_{\text{trans-Stilbene}}} = 2.25 \pm 0.10$						

Table 7. Relative rates of disappearance of 9-chloroanthracene to trans-stilbene.

Conditions: 97 hrs at 70.0°
 Initial mmoles BrCCl₃: 25.64
 Mmoles benzene: 38.27
 Mmoles p-dibromobenzene: 0.5205

Run No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% r x n	$\frac{k_{9\text{-Chloroanth}}}{k_{\text{trans-Stilbene}}}$
1	9-Chloroanth	0.5506	0.4043	0.1463	26.57	2.352
	<u>trans</u> -Stilbene	1.015	0.8902	0.1248	12.30	
2	9-Chloroanth	0.5506	0.4137	0.1369	24.87	2.210
	<u>trans</u> -Stilbene	1.015	0.8918	0.1232	12.14	
3	9-Chloroanth	0.5506	0.4174	0.1332	24.19	2.239
	<u>trans</u> -Stilbene	1.015	0.8970	0.1180	11.63	
4	9-Chloroanth	0.5506	0.3969	0.1537	27.91	2.579
	<u>trans</u> -Stilbene	1.015	0.8940	0.1210	11.92	
5	9-Chloroanth	0.5506	0.3728	0.1778	32.30	2.317
	<u>trans</u> -Stilbene	1.015	0.8577	0.1573	15.50	
6	9-Chloroanth	0.5506	0.4117	0.1389	25.22	2.177
	<u>trans</u> -Stilbene	1.015	0.8882	0.1268	12.49	
7	9-Chloroanth	0.5506	0.4027	0.1479	26.86	2.285
	<u>trans</u> -Stilbene	1.015	0.8852	0.1298	12.79	
Average $\frac{k_{9\text{-Chloroanth}}}{k_{\text{trans-Stilbene}}} = 2.31 \pm 0.09$						

Table 8. Relative rates of disappearance of anthracene to trans-stilbene.

Conditions: 97.25 hrs at 70.0°
 Initial mmoles BrCCl₃: 25.06
 Mmoles benzene: 37.75
 Mmoles p-dibromobenzene: 0.5383

Run No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% r x n	$\frac{k_{\text{Anthracene}}}{k_{\text{trans-Stilbene}}}$
1	Anthracene	0.5426	0.3272	0.2154	39.70	5.776
	<u>trans</u> -Stilbene	1.022	0.9364	0.0856	8.38	
2	Anthracene	0.5426	0.3357	0.2069	38.14	5.177
	<u>trans</u> -Stilbene	1.022	0.9314	0.0905	8.86	
3	Anthracene	0.5426	0.3723	0.1703	31.39	3.923
	<u>trans</u> -Stilbene	1.022	0.9283	0.0936	9.16	
4	Anthracene	0.5426	0.3184	0.2242	41.32	5.566
	<u>trans</u> -Stilbene	1.022	0.9287	0.0933	9.13	
5	Anthracene	0.5426	0.3978	0.1448	26.68	3.774
	<u>trans</u> -Stilbene	1.022	0.9414	0.0806	7.89	
6	Anthracene	0.5426	0.3375	0.2051	37.80	4.030
	<u>trans</u> -Stilbene	1.022	0.9085	0.1135	11.11	
7	Anthracene	0.5426	0.4001	0.1425	26.27	3.422
	<u>trans</u> -Stilbene	1.022	0.9349	0.0871	8.52	

$$\text{Average } \frac{k_{\text{Anthracene}}}{k_{\text{trans-Stilbene}}} = 4.52 \pm 0.84$$

$$\text{Per active position: } \frac{k_{\text{Anthracene}}}{k_{\text{trans-Stilbene}}} = 2.26 \pm 0.42$$

Table 9. Relative rates of disappearance of 9-phenylanthracene to trans-stilbene.

Conditions: 96 hrs at 70.0°
 Initial mmoles BrCCl₃: 25.12
 Mmoles benzene: 37.63
 Mmoles p-dibromobenzene: 0.5459

Run No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% r x n	$\frac{k_{9\text{-Phenylanth}}}{k_{\text{trans-Stilbene}}}$
1	9-Phenylanth	0.5045	0.3455	0.1590	31.52	4.207
	<u>trans</u> -Stilbene	1.007	0.9203	0.0867	8.61	
2	9-Phenylanth	0.5045	0.3869	0.1176	23.31	4.953
	<u>trans</u> -Stilbene	1.007	0.9544	0.0526	5.22	
3	9-Phenylanth	0.5045	0.2918	0.2127	42.16	7.090
	<u>trans</u> -Stilbene	1.007	0.9322	0.0748	7.43	
4	9-Phenylanth	0.5045	0.3320	0.1725	34.20	4.210
	<u>trans</u> -Stilbene	1.007	0.9117	0.0953	9.46	
5	9-Phenylanth	0.5045	0.3171	0.1874	37.15	3.921
	<u>trans</u> -Stilbene	1.007	0.8945	0.1125	11.17	
6	9-Phenylanth	0.5045	0.3824	0.1221	24.20	5.107
	<u>trans</u> -Stilbene	1.007	0.9538	0.0532	5.28	
7	9-Phenylanth	0.5045	0.3530	0.1515	30.02	6.677
	<u>trans</u> -Stilbene	1.007	0.9545	0.0525	5.21	
Average		$\frac{k_{9\text{-Phenylanth}}}{k_{\text{trans-Stilbene}}} = 5.17 \pm 0.98$				

Table 10. Relative rates of disappearance of 9-isopropylanthracene to trans-stilbene.

Conditions: 120 hrs at 70.0°
 Initial mmoles BrCCl₃: 25.08
 Mmoles benzene: 37.61
 Mmoles p-dibromobenzene: 0.5231

Run No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Related (mmoles)	% r x n	$\frac{k_{9\text{-Isopropylanth}}}{k_{\text{trans-Stilbene}}}$
1	9-Isopropylanth	0.5100	0.2842	0.2258	44.27	5.529
	<u>trans</u> -Stilbene	1.036	0.9321	0.1039	10.03	
2	9-Isopropylanth	0.5100	0.3164	0.1936	37.97	5.767
	<u>trans</u> -Stilbene	1.036	0.9536	0.0824	7.95	
3	9-Isopropylanth	0.5100	0.3449	0.1651	32.38	4.949
	<u>trans</u> -Stilbene	1.036	0.9573	0.0787	7.60	
4	9-Isopropylanth	0.5100	0.3446	0.1654	32.43	4.123
	<u>trans</u> -Stilbene	1.036	0.9420	0.0940	9.07	
5	9-Isopropylanth	0.5100	0.2540	0.2560	50.19	6.948
	<u>trans</u> -Stilbene	1.036	0.9371	0.0989	9.55	
6	9-Isopropylanth	0.5100	0.2395	0.2705	53.04	5.018
	<u>trans</u> -Stilbene	1.036	0.8912	0.1448	13.98	

$$\text{Average } \frac{k_{9\text{-Isopropylanth}}}{k_{\text{trans-Stilbene}}} = 5.39 \pm 0.69$$

Table 11. Relative rates of disappearance of 9-ethylanthracene to trans-stilbene.

		Conditions: 100 hrs at 70.0°			Conditions: 122 hrs at 70.0°		
		Initial mmoles BrCCl ₃ : 25.07			Initial mmoles BrCCl ₃ : 25.04		
		Mmoles benzene: 37.69			Mmoles benzene: 37.63		
		Mmoles <u>p</u> -dibromobenzene: 0.5163			Mmoles <u>p</u> -dibromobenzene: 0.5112		
		(Runs 1-5)			(Runs 6-10)		
Run No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% r x n	$\frac{k_{9\text{-Ethylanth}}}{k_{\text{trans-Stilbene}}}$	
1	9-Ethylanth	0.5087	0.3105	0.1982	38.96	6.733	
	<u>trans</u> -Stilbene	0.9709	0.9023	0.0686	7.07		
2	9-Ethylanth	0.5087	0.2846	0.2241	44.05	7.433	
	<u>trans</u> -Stilbene	0.9709	0.8979	0.0730	7.52		
3	9-Ethylanth	0.5087	0.3435	0.1652	32.48	6.542	
	<u>trans</u> -Stilbene	0.9709	0.9143	0.0566	5.83		
4	9-Ethylanth	0.5087	0.3489	0.1598	31.42	8.683	
	<u>trans</u> -Stilbene	0.9709	0.9296	0.0413	4.25		
5	9-Ethylanth	0.5087	0.3221	0.1866	36.69	9.193	
	<u>trans</u> -Stilbene	0.9709	0.9238	0.0471	4.85		
6	9-Ethylanth	0.5015	0.2644	0.2371	47.28	5.028	
	<u>trans</u> -Stilbene	1.022	0.8998	0.1222	11.96		
7	9-Ethylanth	0.5015	0.2294	0.2721	54.26	9.484	
	<u>trans</u> -Stilbene	1.022	0.9410	0.0809	7.92		
8	9-Ethylanth	0.5015	0.2429	0.2586	51.57	7.938	
	<u>trans</u> -Stilbene	1.022	0.9328	0.0892	8.73		
9	9-Ethylanth	0.5015	0.2278	0.2738	54.57	8.008	
	<u>trans</u> -Stilbene	1.022	0.9261	0.0959	9.38		
10	9-Ethylanth	0.5015	0.2689	0.2326	46.39	7.594	
	<u>trans</u> -Stilbene	1.022	0.9415	0.0805	7.88		

Average $\frac{k_{9\text{-Ethylanth}}}{k_{\text{trans-Stilbene}}} = 7.66 \pm 1.00$

Table 12. Relative rates of disappearance of 9-methylanthracene to trans-stilbene.

Conditions: 117.5 hrs at 70.0°
 Initial mmoles BrCCl₃: 25.05
 Mmoles benzene: 37.56
 Mmoles p-dibromobenzene: 0.5120

Run No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% r x n	$\frac{k_{9\text{-Methylanth}}}{k_{\text{trans-Stilbene}}}$
1	9-Methylanth	0.5108	0.1391	0.3717	72.77	14.198
	<u>trans</u> -Stilbene	0.9725	0.8874	0.0851	8.75	
2	9-Methylanth	0.5108	0.2043	0.3065	60.01	13.497
	<u>trans</u> -Stilbene	0.9725	0.9087	0.0638	6.56	
3	9-Methylanth	0.5108	0.2233	0.2875	56.29	14.781
	<u>trans</u> -Stilbene	0.9725	0.9196	0.0529	5.44	
4	9-Methylanth	0.5108	0.2029	0.3079	60.28	18.580
	<u>trans</u> -Stilbene	0.9725	0.9253	0.0472	4.85	
5	9-Methylanth	0.5108	0.2528	0.2580	50.50	18.456
	<u>trans</u> -Stilbene	0.9725	0.9361	0.0364	3.74	
6	9-Methylanth	0.5108	0.2820	0.2288	44.79	13.505
	<u>trans</u> -Stilbene	0.9725	0.9307	0.0418	4.30	

$$\text{Average } \frac{k_{9\text{-Methylanth}}}{k_{\text{trans-Stilbene}}} = 15.50 \pm 2.01$$

Table 13. Relative rates of disappearance of 9-methoxyanthracene to trans-stilbene.

Conditions: 77 hrs at 70.0°
 Initial mmoles BrCCl₃: 25.82
 Mmoles benzene: 38.50
 Mmoles p-dibromobenzene: 0.5129

Run No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% r x n	$\frac{k_{9\text{-Methoxyanth}}}{k_{\text{trans-Stilbene}}}$
1	9-Methoxyanth	0.5192	0.3309	0.1883	36.26	12.317
	<u>trans</u> -Stilbene	1.072	1.034	0.0385	3.59	
2	9-Methoxyanth	0.5192	0.2847	0.2345	45.17	10.785
	<u>trans</u> -Stilbene	1.072	1.014	0.0581	5.42	
3	9-Methoxyanth	0.5192	0.2896	0.2296	44.22	10.918
	<u>trans</u> -Stilbene	1.072	1.016	0.0558	5.21	
4	9-Methoxyanth	0.5192	0.2857	0.2335	44.98	15.430
	<u>trans</u> -Stilbene	1.072	1.031	0.0407	3.80	
5	9-Methoxyanth	0.5192	0.3179	0.2013	38.77	12.919
	<u>trans</u> -Stilbene	1.072	1.032	0.0399	3.72	
Average		$\frac{k_{9\text{-Methoxyanth}}}{k_{\text{trans-Stilbene}}} = 12.47 \pm 1.36$				